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This Week's Citation Classic

Sroog C E, Endrey A L, Abramo S V, Berr C E, Edwards W M & Olivier K L.
Aromatic polypyromellitimides from aromatic polyamic acids.
J. Polym. Sci. **3**:1373-90, 1965.
[Film and Plastics Depts., E.I. Du Pont de Nemours, Experimental Station Laboratory, Wilmington, DE]

This paper describes the synthesis of aromatic poly(amic-acids) as a synthetic route to high-melting intractable polyimides. Included are essentials of synthesis, conversion to imide, fundamental structural information, and properties of both the unstable poly(amic-acid) and the final stable polyimide. [The *SCI*® indicates that this paper has been cited over 180 times since 1965.]

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"This work began among a group of young chemists, newly employed at a Du Pont laboratory. Informal discussions were held on reaction routes to high polymers which involved unstable intermediates. We were aware that traditional direct polymerization routes had led, among other polymer types, to aromatic polyimides which were intractable high-melting powders, whose structures were not understood, and were of no utility. In fact, nobody was particularly interested in them. However, in thinking about unstable intermediates, it seemed natural to consider the poly(amic-acid), which was predicted to be unstable, as a route to the final polyimide film or fiber which was expected to be stable. In more enthusiastic moments, as confidence grew, it seemed possible to replace 'aging' cellophane facilities with a new material, which I anticipated would also require some type of solvent processing.

"About this time, Du Pont opened a new exploratory laboratory in Wilmington, and I had the responsibility of organizing its new programs. This work was almost first on the list, and we began in a research environment of strong support for what was then recognized as very novel research.

"The work on poly(amic-acid) synthesis went well but problems arose in cyclization to polyimide. Publications by ML. Bender[1-2] described kinetics of hydrolytic instability of monomeric phthalamic-acid in water. Our thinking about these and other data helped us to improve the conversion to imide in particular to avoid a water medium. We succeeded in the conversion and obtained very high-melting, but brittle films. These were difficult to dissolve with resulting low viscosities in our analytical solutions. This led to some controversy as to whether we were really obtaining high polymer, or simply low-molecular weight materials of undefined structure and no utility. We persisted and were finally able to obtain very tough polyimide films. Our initial product expectation was for materials of high rigidity resulting from the multi-ring structure. As it turned out, the polyimides were not all that rigid but we were well aware of the need for thermally stable, high-melting materials. We checked the thermal stability, which proved to be outstanding, and we were on our way.

"The work on polyimides demonstrated that unstable intermediates could indeed be a route to previously unavailable, intractable materials, and spawned a whole generation of activity on a bewildering variety of heterocyclic polymers. Interest in this paper related to the scientific novelty, and the unusual polyimide properties. The polyimides as films, coatings, and plastics, have supported demanding end-uses in the electrical, oil, and aerospace industries. We thereby have the double satisfaction of both scientific and economic accomplishment. It must be noted, however, that despite this satisfaction, we have not learned to use cellophane facilities to process polyimides, nor is the polyimide now any easier to dissolve. I published a review in this field in 1976."[3]

1. **Bender M L.** General acid-base catalysis in the intramolecular hydrolysis of phthalamic acid. *J. Amer. Chem. Soc.* **79**:1258-9. 1957.
2. **Bender M L, Chow Y L & Chloupek** F. Intramolecular catalysis of hydrolytic reactions. II. The hydrolysis of phthalamic acid. *J. Amer. Chem. Soc.* **80**:5380-4. 1958.
3. **Sroog C E.** Polyimides. *Macromol. Rev. J. Polym. Sci.* **11**:161-208. 1976.